Metal selenide nanocrystals prepared by processing bulk materials in hot hexadecylamine

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Abstract. Metal selenide (CdSe, CoSe and $Cu_{1.8}Se$) nanocrystals were synthesized by the injection of the bulk materials into hexadecylamine (HDA) at 160°C for 10 minutes. Ultraviolet-visible (UV-vis) spectra showed that the excitonic peaks are blue-shifted from those of their bulk counter-parts which are indicative of the quantum confinement effect. Photoluminescence (PL) spectra showed the NCs emit and their emission peaks were red-shifted from the respective absorption maxima. The synthesized metal selenide NCs were spherical as observed in transmission electron microscopy (TEM) images. The results showed that the method of processing bulk materials in hot HDA can be adapted to synthesize various metal selenide nanocrystals.

1. Introduction

Metal selenide (MSe) nanocrystals (NCs) have received much attention recently due to their unique optical and structural properties. MSe NCs (e.g. cadmium selenide, copper selenide and cobalt selenide) have interesting bulk band-gaps, in the range 1.38 eV – 2.2 eV, which meet the requirement of the Shockley-Quessier limit on the optimum efficiency of a single junction solar cell [1]. One of the advantages of NCs over their bulk counterparts is the ability to engineer their band-gaps by varying their sizes. The size variation is achieved by controlling variables such as temperature and time during synthesis. Hence, these materials are very attractive for incorporation into photovoltaic devices [2], among other applications such as gas sensors [3] and therapeutics [4]. Additionally, the optical and electrical properties of the nanocrystals are influenced by their shapes such as rods, fractals, bipods, tripods, dots, tubes, etc. These various morphologies have been synthesized by a range of methods including the aqueous route, organometallic, hydrothermal, solvothermal, microwave, chemical vapour deposition, etc. The type of metal precursors also has an influence on the morphology of the resulting NCs. For example, cadmium chloride and cadmium carbonate produced spherical and rod-shaped CdSe NCs, respectively. when used as cadmium precursors [5]. Apart from cadmium selenide, both copper selenide and cobalt selenide nanocrystals exist in a range of compositions. For example, cobalt selenide may crystallize in stoichiometries such as CoSe, $CoSe_2$, $Co_{0.85}Se$, Co_3Se_4 and Co_2Se_3 while those for copper selenide are CuSe, $Cu_{2-x}Se$, Cu_2Se and Cu_3Se_2. Cobalt selenide is known to be metallic conductor which behaves as a Pauli paramagnet in its ground state with a Curie temperature (Tc) of 124 K [6] while copper selenide is a p-type material. In this study, three metal selenides, i.e. cadmium, copper and cobalt selenide nanocrystals were synthesized successfully by the same method, using same reaction condition.

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2. Experimental

2.1. Preparation of the bulk material

Sodium hydrogen selenide (NaHSe) solution was freshly prepared in a three-necked round-bottom flask by the reduction of the selenium powder (12.5 mmol, Se) with sodium borohydride (26.5 mmol, $NaBH_4$) in 50 ml de-ionized water as solvent. A clear solution was obtained after an hour. Cadmium chloride solution was prepared in a beaker by dissolving 12.5 mmol $CdCl_2$ in 50 ml of deionised water and added to the clear NaHSe solution and the reaction was stirred continuously for 30 min. Methanol was added into the flask to induce flocculation and bulk CdSe was recovered by centrifugation at 3000 rpm for 5 minutes. Similar procedure was used to prepare bulk Cu_xSe_y and Co_xSe_y.

2.2 Preparation of the nanocrystals

Bulk metal-selenide (50 mg) was dispersed in 5 ml trioctylphosphine (TOP) for an hour under intense magnetic stirring and inert atmosphere. This dispersion was subsequently injected into HDA (6 g) heated to 160°C and the reaction was held at this temperature for 10 minutes. The resulting product was allowed to cool below 100°C. A mixture of toluene (4ml) and ethanol (100 ml) was then added to the flask to induce flocculation. The products were recovered by centrifugation at 3000 rpm for 10 minutes.

2.3 Characterization techniques

The optical properties of the materials were determined by placing the chloroform dispersion of the NCs into the quartz cuvettes. UV-Visible spectroscopy (AnalytikJena SPECORD 50) was used to determine the absorption properties of the NCs and the StellarNet miniature spectrofluorometer, equipped with 395 nm LED as an excitation source, was used to determine the emission properties of the NCs. The morphology of the nanocrystals was determined on Technai G^2 TEM Spirit operated at 200 kV. TEM samples were prepared by drop-casting the NCs dispersion in chloroform onto the carbon-coated copper grids and allowed to dry at room temperature. The crystal structures were determined using Bruker D2 Phaser Powder X-ray diffractometer using Co (1.78898 nm) radiation.

3. Results and discussion

3.1 Structural properties

The synthesized samples were characterized by the XRD technique to determine their crystal phases and purity. Figure 1 shows the diffraction patterns of the metal (Cd, Cu and Co) selenide nanocrystals synthesized in this study. Figure 1(a) shows three distinct diffraction peaks corresponding to (111), (220) and (311) lattice planes which could be indexed to face-centred cubic (*fcc*) phase of CdSe (PDF card number 019-0191). No impurity peaks were detected by the XRD. The diffraction pattern for copper selenide NCs is shown in Figure 1 (b). All the diffraction peaks (111), (200), (220), (311), (400), and (311) shown in Figure 1 (b) can be indexed to the face-centred cubic (*fcc*) berzelianite $Cu_{1.8}Se$ (PDF card number 071-0044). The cobalt selenide sample shows Bragg reflections (101), (102), (110) and (103) depicted in Figure 1 (c) which can be indexed to hexagonal close-packed (*hcp*) phase of freboldite CoSe (PDF card number 089-2004).

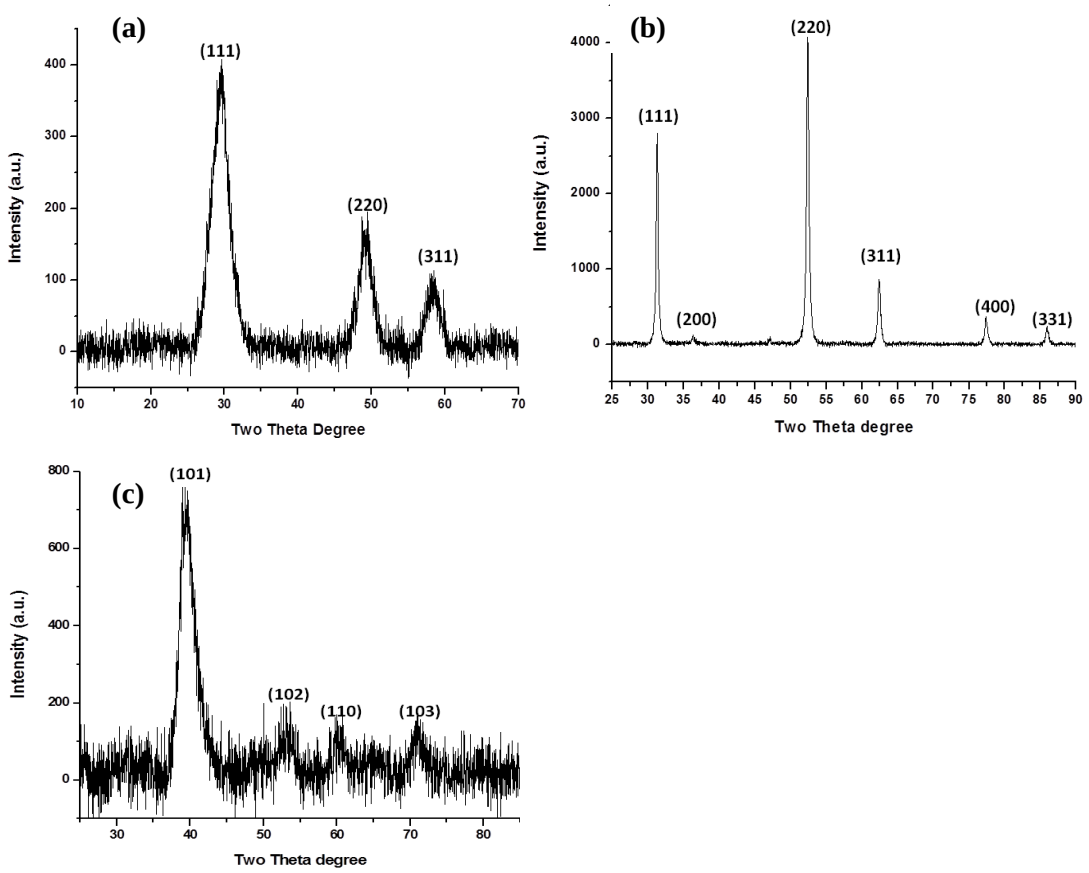
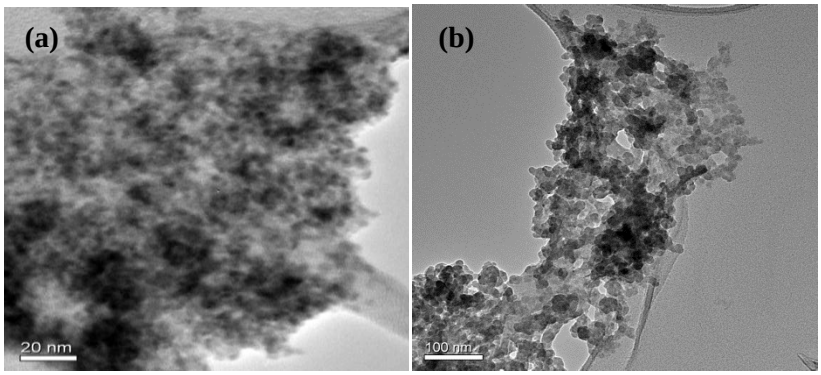


Figure 1. XRD patterns for HDA-capped (a) CdSe, (b) $Cu_{1.8}Se$ and (c) CoSe NCs synthesized at 160°C for 10 minutes.

TEM images of the synthesized metal selenide NCs are shown in Figure 2. These images confirmed the successful synthesis of the metal selenide by the injection of bulk materials into hot HDA. Spherical NCs were obtained for CdSe, $Cu_{1.8}Se$ and CoSe NCs as depicted in Figure 2 (a)-(c), respectively. Evident from the TEM images is the spherical morphology of the NCs and some chaining effect due to the presence of HDA on the surfaces of the NCs which prevented the nanocrystals from agglomerating. The average NCs sizes were estimated from the TEM images and were found to be 2.8 nm for CdSe, 16.3 nm and 3.5 nm for $Cu_{1.8}Se$ and CoSe NCs, respectively. The larger $Cu_{1.8}Se$ NCs size is consistent with the sharp XRD peaks observed for this sample while broader XRD peaks for CdSe and CoSe NCs indicated small nanocrystals size as confirmed by TEM results.



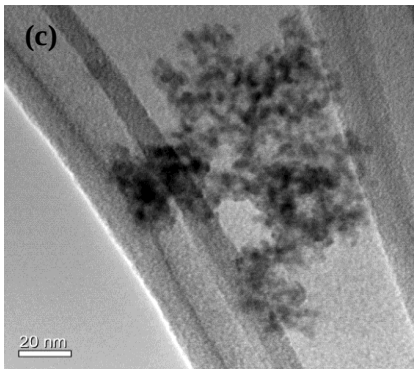


Figure 2. TEM images for CdSe (a), $Cu_{1.8}Se$ (b), and CoSe (c) synthesized in HDA at 160°C.

Optical properties of the synthesized nanocrystals are depicted in Figure 3 (a)-(c). Absorption spectrum for CdSe NCs show a sharp excitonic peak centered at ~ 540 nm due to the first electronic transition (1s–1s) of the CdSe NCs [7] and a PL peak, centred at ~ 600 nm, which is red-shifted absorption peak. The absorption peak of the CdSe NCs is blue shifted from the absorption bulk material at 716 nm which is due to the quantum-confinement effect. Similar results were obtained for both $Cu_{1.8}Se$ and CoSe NCs which also showed blue-shifted absorption peaks relative to their bulk counter-parts due to the quantum confinement effect. However, the absorption profile of these NCs showed broad excitonic peaks which indicate a broad size distribution.

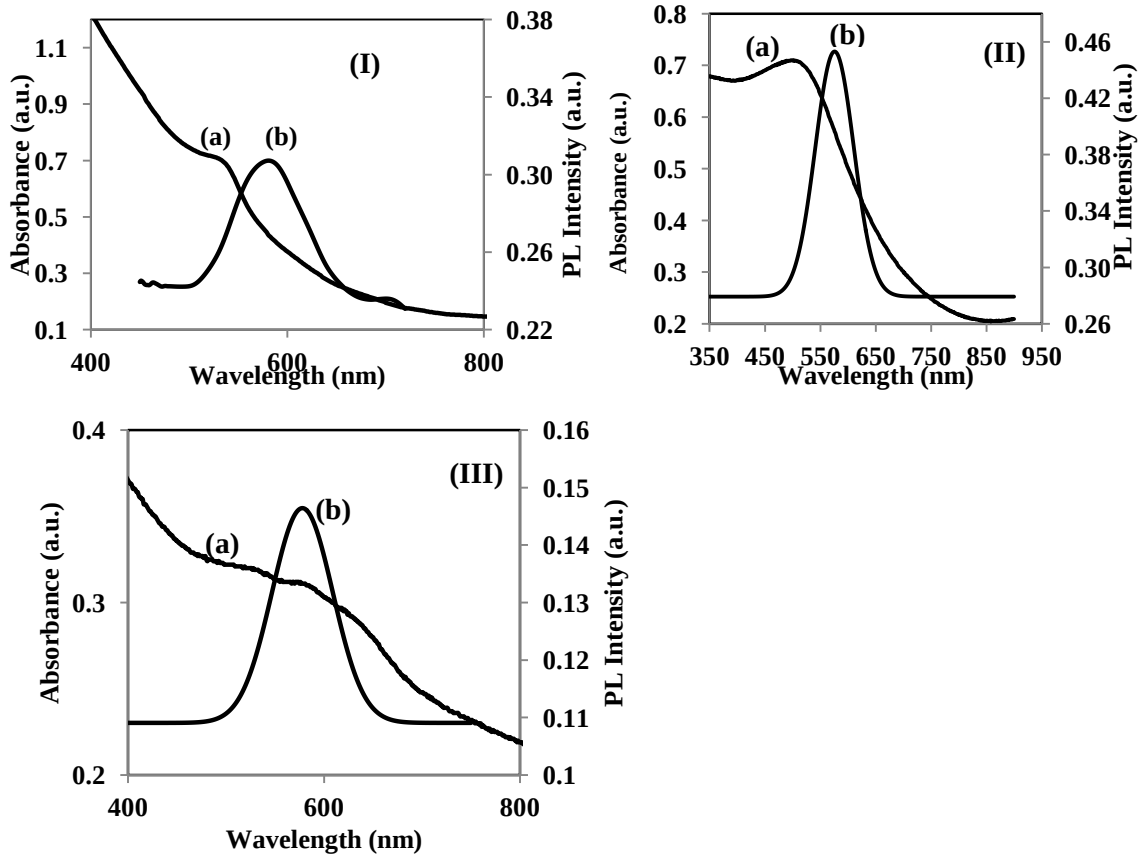


Figure 3. Absorption (a) and emission (b) spectra for HDA-capped CdSe NCs (I), $Cu_{1.8}Se$ (II) and CoSe (III), synthesized at 160°C for 10min.

4. Conclusions

Nanocrystalline CdSe, CoSe and $Cu_{1.8}Se$ materials were synthesized by the bulk injection into hot HDA at low temperatures. Both particles showed quantum confinement effect as their absorption spectra shifted to higher energies compared to their bulk counter-parts. The synthesis method use produced smaller diameters for CdSe and CoSe NCs whereas larger NCs were obtained for $Cu_{1.8}Se$. XRD patterns showed these NCs were obtained as pure products as no impurity materials were detected. This study showed MSe NCs can be synthesized using the same method and reaction conditions.

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References

[1] W. Shockley and H. J. Queisser, Journal of Applied Physics 32 (1961) 510.
[2] I. J. Kramer and E. H. Sargent, ACS Nano 5 (2011) 8506.
[3] O. V. Vassiltsova, Z. Zhao, M. A. Petrukhina, and M. A. Carpenter, Sensors and Actuators B: Chemical 123 (2007) 522.
[4] C. M. Hessel, V. P. Pattani, M. Rasch, M. G. Panthani, B. Koo, J. W. Tunnell, and B. A. Korgel, Nano Letters 11 (2011) 2560.
[5] N. N. Maseko, N. Revaprasadu, V. S. R. R. Pullabhotla, R. Karthik, and P. O'Brien, Materials Letters 64 (2010) 1037.
[6] W. Maneeprakorn, M. A. Malik, and P. O'Brien, Journal of Materials Chemistry 20 (2010) 2329.
[7] O. Samuel Oluwafemi and N. Revaprasadu, New Journal of Chemistry 32 (2008) 1432.